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| <p>(54) Title: PRODUCTION OF DIHALOMETHANES CONTAINING FLUORINE AND AZEOTROPES OF DIHALOMETHANES CONTAINING CHLORINE WITH HF</p> <p>(57) Abstract</p> <p>A process for producing difluoromethane is disclosed which includes the step of contacting a gaseous mixture containing CH_2Cl_2 and hydrogen fluoride with a catalyst containing a catalytically effective amount of trivalent chromium supported on a carbon having an ash content of less than 0.5 percent by weight, at a temperature of from about 180 °C to about 375 °C. The catalyst and temperature conditions of this process allow the concurrent reaction CCl_3CF_3 with HF to form CCl_2FCF_3, CH_2ClF and unreacted CH_2Cl_2, each of which may be recovered as an azeotrope with HF, may be recycled.</p> | | |

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TITLE

PRODUCTION OF DIHALOMETHANES CONTAINING FLUORINE
AND AZEOTROPES OF DIHALOMETHANES CONTAINING
CHLORINE WITH HF

5

FIELD OF THE INVENTION

This invention relates to the production of halocarbons and their azeotropes and more particularly to the production of difluoromethane (i.e., CH_2F_2 or HFC-32) and azeotropes of chlorine-containing precursors thereof (i.e., CH_2ClF or HCFC-31, and CH_2Cl_2) with HF.

BACKGROUND

Chlorofluorocarbons (i.e., CFCs) are compounds containing only carbon, fluorine and chlorine. Various CFCs have been used for many years as refrigerants, heat transfer media, foam expansion agents, aerosol propellants, solvents and power cycle working fluids. However, there has been recent concern that CFCs may be detrimental to the Earth's ozone layer. Consequently, there is a worldwide effort to find alternative compounds which contain fewer or preferably no chlorine substituents. The hydrofluorocarbon difluoromethane has been proposed as a replacement for some CFCs, particularly, in refrigeration, air-conditioning and other applications (see e.g., European Patent Application Publication No. 508,660 A1). Accordingly, there is interest in developing efficient processes for the production of HFC-32.

Japanese Patent Publication 59-225131 discloses preparation of HFC-32 by reacting dichloromethane with HF in the vapor phase at 200 to 500°C in the presence of a catalyst which consists of chromium fluoride or which has been obtained by molding a mixture of chromium fluoride and a carrier or by supporting chromium fluoride on a carrier. Chromium fluoride may be obtained by fluorinating a chromium-containing compound.

Immersion of activated carbon in a solution of chromium chloride, followed by treatment with HF is disclosed (see e.g., Example 2). It is well known that activated carbon typically has an ash content comprising metal-
5 containing compounds (e.g., potassium and sodium oxides) and other impurities (see e.g., M. Smisek et al. "Active Carbon", pages 61-70 (1970) and J. W. Hassler "Activated Carbon", pages 344-345 (1963)).

1,1-Dichlorotetrafluoroethane (i.e., CCl_2FCF_3 or
10 CFC-114a) is of interest as an intermediate for producing 1,1,1,2-tetrafluoroethane (i.e., $\text{CF}_3\text{CH}_2\text{F}$ or HFC-134a). $\text{CF}_3\text{CH}_2\text{F}$ can be obtained by the catalytic hydrogenolysis of CCl_2FCF_3 using a supported metal hydrogenation catalyst (see e.g., C. Gervasutti et al.,
15 J. Fluorine Chem., 1981/82, 19, pgs. 1-20). The HFC-134a is an environmentally acceptable potential replacement for CFC refrigerants, blowing agents, aerosol propellants and sterilants that are implicated in the destruction of stratospheric ozone.

20 SUMMARY OF THE INVENTION

The present invention provides a process for producing difluoromethane. The process comprises the step of contacting a gaseous mixture containing CH_2Cl_2 and hydrogen fluoride with a catalyst containing a
25 catalytically effective amount of trivalent chromium supported on a carbon having an ash content of less than 0.5 percent by weight, at a temperature of from about 180°C to about 375°C . The catalyst and temperature conditions of this process allow the concurrent reaction
30 of 1,1,1-trichlorotrifluoroethane (i.e., CCl_3CF_3 or CFC-113a) with HF to form CFC-114a. CH_2ClF and unreacted CH_2Cl_2 , each of which may be recovered as an azeotrope with HF, may be recycled.

The present invention also provides compositions
35 which consist essentially of hydrogen fluoride in

combination with an effective amount of a compound selected from the group consisting of CH_2Cl_2 and CH_2ClF to form an azeotrope or azeotrope-like composition with hydrogen fluoride, said composition containing from
5 about 5 to 29 mole% CH_2Cl_2 or from about 58 to 65 mole% CH_2ClF .

DETAILED DESCRIPTION

The present invention provides a process for the vapor-phase catalytic fluorination of CH_2Cl_2 to CH_2F_2 .
10 The process may be used for the vapor-phase catalytic fluorination of mixtures of CH_2Cl_2 and CCl_3CF_3 to produce both CH_2F_2 and CCl_2FCF_3 . The process of this invention employs catalyst compositions comprising trivalent chromium. In addition to a catalytically effective
15 amount of trivalent chromium such fluorination catalysts can include other components to increase catalyst activity and/or life such as one or more divalent metal cations (e.g., zinc, magnesium and/or cobalt). While unsupported trivalent chromium catalysts (e.g., Cr_2O_3)
20 or trivalent chromium catalysts supported on non-carbon supports (e.g., on alumina, aluminum fluoride, or magnesium fluoride) may also catalyze the reaction of CH_2Cl_2 to CH_2F_2 , this invention advantageously involves trivalent chromium (e.g., CrCl_3 and/or CrF_3) supported
25 on a carbon which has an ash content of less than 0.5 weight percent. A CrF_3 on carbon is disclosed in U.S. Patent No. 3,632,834, the contents of which are incorporated herein by reference. Catalysts suitable for use in the process of this invention can be prepared
30 in a manner similar to that disclosed in U.S. Patent No. 3,632,834, provided the carbon used has an ash content of less than 0.5 weight percent. Preferred catalysts include a low ash content carbon support (as described herein) containing chromium chloride (CrCl_3),
35 fluorided chromium chloride (e.g., CrCl_3 treated with HF

to produce chromium chlorofluoride(s)), or mixtures of chromium chloride and chromium fluoride (CrF_3). While such low-ash carbon supports may be obtained using a variety of methods, a preferred carbon support is acid-washing activated carbon prior to impregnating it with trivalent chromium. Preferably the chromium content (expressed as CrCl_3) is from about 5 to 60 weight percent of the carbon supported catalyst.

The initial acid treatment typically uses an acid other than hydrofluoric acid. Preferred acids used for the acid treatment contain neither phosphorus nor sulfur. Examples of acids which may be used in the initial acid wash during the catalyst preparation process include organic acids such as acetic acid and inorganic acids such as hydrochloric acid or nitric acid. Preferably, hydrochloric acid or nitric acid is used. The second acid treatment, when employed, advantageously uses hydrofluoric acid. Preferably, the carbon is treated with acid such that after such treatment the carbon contains less than about 0.2% by weight ash.

Commercially available carbons which may be treated with acids to provide suitable supports include those sold under the following trademarks: Darco™, Nuchar™, Columbia SBV™, Columbia MBV™, Columbia MBQ™, Columbia JXC™, Columbia CXC™, Calgon PCB™, Norit™ and Barnaby Cheny NB™. The carbon support can be in the form of powder, granules, or pellets, etc.

The acid treatment may be accomplished in several ways. A suitable procedure is as follows. A carbon support is soaked overnight with gentle stirring in a 1 molar solution of the acid prepared in deionized water. The carbon support is then separated and washed with deionized water until the pH of the washings is about 3. Preferably, the carbon support is then soaked

again with gentle stirring in a 1 molar solution of the acid prepared in deionized water for 12 to 24 hours. The carbon support is then finally washed with deionized water until the washings are substantially free of the anion of the acid (e.g., Cl^- or NO_3^-), when tested by standard procedures. The carbon support is then separated and dried at about 120°C . The washed carbon is then soaked, if necessary, in 1 molar HF prepared in deionized water for about 48 hours at room temperature with occasional stirring. The carbon support is separated and washed repeatedly with deionized water until the pH of the washings is greater than 4. The carbon support is then dried followed by calcination at 300°C for about 3 hours in air prior to its use as a support. Reference is made to U.S. Patent No. 5,136,113 for further details relating to producing acid-washed carbon catalysts.

Typically, where the starting material to be fluorinated consists essentially of CH_2Cl_2 , the molar ratio of HF added to CH_2Cl_2 starting material added (whether or not CH_2ClF , unreacted CH_2Cl_2 and/or HF are also recycled) ranges from about 0.5:1 to about 10:1, and is preferably from about 1:1 to 8:1, more preferably about 2:1 to 6:1. Typically, where the starting material to be fluorinated consists essentially of a mixture of CH_2Cl_2 and CCl_3CF_3 , the molar ratio of HF added to the total amount of CH_2Cl_2 and CCl_3CF_3 starting material added typically ranges from about 0.5:1 to about 10:1, and is preferably from about 1:1 to 8:1. Typically, the molar ratio of CH_2Cl_2 to CCl_3CF_3 in mixtures ranges from about 1:9 to about 9:1.

Suitable reaction temperatures range from about 180°C to about 375°C . Preferably, the reaction temperature is in the range of from about 200°C to about 350°C . Pressure is not critical. Atmospheric and

superatmospheric pressures (e.g., from about 100 kPa to about 7000 kPa) are the most convenient and are therefore preferred.

5 The fluorination reaction is performed in the vapor phase using well known chemical engineering practice, which includes continuous, semi-continuous or batch operations. The fluorination reaction may be done in the presence of inert gases e.g., nitrogen, helium or argon.

10 The reaction product stream can be treated in accordance with any of the techniques known to the art for separating the desired fluorination product from by-product hydrogen chloride, unreacted hydrogen fluoride, chlorofluoromethane and other minor
15 by-products. For example, HFC-32 can be separated from the other components of the reaction products by distillation. It has been found that during this distillation that chlorofluoromethane (i.e., CH_2ClF or HCFC-31) can form a binary azeotrope with HF. It has
20 also been found that CH_2Cl_2 can form a binary azeotrope with HF. Accordingly, the CH_2ClF and unreacted CH_2Cl_2 can each be recovered as a composition consisting essentially of an azeotrope thereof and HF, using
25 distillation. Further discussion of these azeotropes is provided below.

Alternatively, the product stream may be scrubbed with water or aqueous alkali to remove hydrogen halides, dried with a drying agent, such as silica gel or a
30 molecular sieve adapted to such purpose and recovered. Preferably, CH_2ClF and unreacted CH_2Cl_2 and/or their azeotropes with hydrogen fluoride are recycled to the fluorination reactor.

The reactors, separators and their associated feed lines, effluent line and associated units should be
35 constructed of materials resistant to hydrogen fluoride,

hydrogen chloride and chlorine. Typical materials of construction, well-known to the fluorination art, include stainless steels, in particular of the austenitic type, and the well-known high nickel alloys, such as
5 Monel® nickel-copper alloys, Hastelloy® nickel-based alloys and, Inconel® nickel-chromium alloys. Also suitable for reactor fabrication are such polymeric plastics as polytrifluorochloroethylene and polytetrafluoroethylene, generally used as linings.

10 As noted above, the present invention provides a composition which consists essentially of hydrogen fluoride and an effective amount of a compound selected from the group consisting of CH_2Cl_2 and CH_2ClF to form an azeotropic composition with hydrogen fluoride. By
15 effective amount is meant an amount which, when combined with HF, results in the formation of an azeotrope or azeotrope-like mixture. As recognized in the art, an azeotrope or an azeotrope-like composition is an admixture of two or more different components which,
20 when in liquid form under given pressure, will boil at a substantially constant temperature, which temperature may be higher or lower than the boiling temperatures of the components, and which will provide a vapor composition essentially identical to the liquid
25 composition undergoing boiling.

For the purpose of this discussion, azeotrope-like composition means a composition that behaves like an azeotrope (i.e., has constant-boiling characteristics or a tendency not to fractionate upon boiling or
30 evaporation). Thus the composition of the vapor formed during boiling or evaporation is the same as or substantially the same as the original liquid composition. Hence, during boiling or evaporation, the liquid composition, if it changes at all, changes only
35 to a minimal or negligible extent. This is to be

contrasted with non-azeotrope-like compositions in which during boiling or evaporation, the liquid composition changes to a substantial degree.

Accordingly, the essential features of an azeotrope or an azeotrope-like composition are that at a given pressure, the boiling point of the liquid composition is fixed and that the composition of the vapor above the boiling composition is essentially that of the boiling liquid composition (i.e., no fractionation of the components of the liquid composition takes place). It is also recognized in the art that both the boiling point and the weight percentages of each component of the azeotropic composition may change when the azeotrope or azeotrope-like liquid composition is subjected to boiling at different pressures. Thus an azeotrope or an azeotrope-like composition may be defined in terms of the unique relationship that exists among components or in terms of the compositional ranges of the components or in terms of exact weight percentages of each component of the composition characterized by a fixed boiling point at a specified pressure. It is also recognized in the art that various azeotropic compositions (including their boiling points at particular pressures) may be calculated (see, e.g., W. Schotte Ind. Eng. Chem. Process Des. Dev. 1980, 19, pp. 432-439). Experimental identification of azeotropic compositions involving the same components may be used to confirm the accuracy of such calculations and/or to modify the calculations at the same or other temperatures and pressures.

Compositions may be formed which consist essentially of azeotropic combinations of hydrogen fluoride with a compound selected from the group consisting of CH_2Cl_2 and CH_2ClF . These include a composition consisting essentially of from about 42 to

about 35 mole percent HF and from about 58 to about 65 mole percent CH_2ClF (which form an azeotrope boiling at a temperature from about -25°C to about 75°C and a pressure between about 55 kPa and about 1700 kPa); and a composition consisting essentially of from about 95 to about 71 mole percent HF and from about 5 to about 29 mole percent CH_2Cl_2 (which form an azeotrope boiling at a temperature from about -50°C to about 110°C and a pressure between about 5 kPa and about 2280 kPa).

To determine the relative volatility of HF with CH_2Cl_2 and with CH_2ClF , the so-called PTx Method was used. In this procedure, the total absolute pressure in a cell of known volume is measured at a constant temperature for various known binary compositions. Use of the PTx Method is described in greater detail in "Phase Equilibrium in Process Design", Wiley-Interscience Publisher, 1970, written by Harold R. Null, on pages 124 to 126, the entire disclosure of which is hereby incorporated by reference. Samples of the vapor and liquid were obtained and analyzed to verify their respective compositions.

These measurements can be reduced to equilibrium vapor and liquid compositions in the cell by an activity coefficient equation model, such as the Non-Random, Two-Liquid (NRTL) equation, to represent liquid phase non-idealities. Use of an activity coefficient equation, such as the NRTL equation, is described in greater detail in "The Properties of Gases and Liquids", 4th Edition, publisher McGraw Hill, written by Reid, Prausnitz and Poling, on pages 241 to 387; and in "Phase Equilibria in Chemical Engineering", published by Butterworth Publishers, 1985, written by Stanley M. Walas, pages 165 to 244; the entire disclosure of each of the previously identified references are hereby incorporated by reference.

Without wishing to be bound by any theory or explanation, it is believed that the NRTL equation can sufficiently predict whether or not mixtures of HF and either CH_2Cl_2 or CH_2ClF behave in an ideal manner, and
5 can sufficiently predict the relative volatilities of the components in such mixtures. Where the relative volatility approaches 1.0 defines the system as forming a near-azeotrope. Where the relative volatility is 1.0 defines the system as forming an azeotrope.

10 It has been found that azeotropes of HCFC-31 and HF are formed at a variety of temperatures and pressures. Between 55 kPa (at a temperature of -25°C) and 1700 kPa (at a temperature of 75°C) azeotropic compositions consisting essentially of HCFC-31 and HF range from
15 about 42 mole percent HF (and 58 mole percent HCFC-31) to about 35 mole percent HF (and 65 mole percent HCFC-31). An azeotrope of HF and CH_2ClF has been found at 20°C and 49.3 psia (340 kPa) consisting essentially of 37.5 mole percent HF and 62.5 mole percent CH_2ClF .
20 Based upon the above findings, it has been calculated that an azeotropic composition of about 42 mole percent HF and 58 mole percent HCFC-31 can be formed at -25°C and 55 kPa and an azeotropic composition of about 35 mole percent HF and 65 mole percent HCFC-31 can be
25 formed at 75°C and 1700 kPa. Accordingly, the present invention provides an azeotrope or azeotrope-like composition consisting essentially of from about 42 to about 35 mole percent HF and from about 58 to 65 mole percent CH_2ClF , said composition having a boiling point
30 from about -25°C at 55 kPa to about 75°C at 1700 kPa.

It has been found that azeotropes of CH_2Cl_2 and HF are formed at a variety of temperatures and pressures. Between 5 kPa (at a temperature of -50°C) and 2280 kPa (at a temperature of 110°C) azeotropic compositions
35 consisting essentially of CH_2Cl_2 and HF range from about

95 mole percent HF (and 5 mole percent CH_2Cl_2) to about 71 mole percent HF (and 29 mole percent CH_2Cl_2). An azeotrope of HF and CH_2Cl_2 has been found at 20°C and 20.8 psia (143 kPa) consisting essentially of 85 mole percent HF and 15 mole percent CH_2Cl_2 . Based upon the above findings, it has been calculated that an azeotropic composition of about 95 mole percent HF and 5 mole percent CH_2Cl_2 can be formed at -50°C and 5 kPa and an azeotropic composition of about 71 mole percent HF and 29 mole percent CH_2Cl_2 can be formed at 110°C and 2280 kPa. Accordingly, the present invention provides an azeotrope or azeotrope-like composition consisting essentially of from about 95 to about 71 mole percent HF and from about 5 to 29 mole percent CH_2Cl_2 , said composition having a boiling point from about -50°C at 5 kPa to about 110°C at 2280 kPa. These azeotropes are considered to be heterogeneous in that two liquid phases are present.

It will be apparent to one of ordinary skill in the art that distillation including azeotropes with HF can typically be run under more convenient conditions than distillation without HF (e.g., where HF is removed prior to distillation).

Practice of the invention will become further apparent from the following non-limiting examples.

EXAMPLES

Activation Procedure

A 5/8" (1.58 cm) I.D. Inconel® nickel alloy reactor was charged with a catalyst and heated to 300°C in a flow of nitrogen (25 mL/min) for about 20 hours. The temperature was reduced to 175°C and a 2:1 molar ratio of nitrogen and HF was started through the reactor (total flow 100 mL/min). After one hour under these conditions, the molar ratio of nitrogen to HF was adjusted to 1:3 and the temperature increased gradually

over a two hour period to 400°C. The reactor was then brought back to the desired operating temperature, the nitrogen flow stopped, and the flow of reactants started.

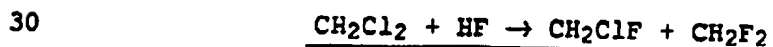
5 Analytical Procedure

The reactor effluent was sampled on-line at various run times (R.T.s) with a Hewlett Packard HP 5890 gas chromatograph using a 20 foot (6.1 m) long, one-eighth inch (0.32 cm) diameter, column containing Krytox™
10 perfluorinated polyether on an inert support and a helium flow of 35 mL/min. Gas chromatographic conditions were 70°C for three minutes followed by temperature programming to 180°C at a rate of 6°C/minute. The table percentages are in area % unless
15 noted otherwise.

Carbons Used

The examples used either Carbon A, a 6 x 16 mesh (about 3.4 mm x 1.2 mm) commercial grade coconut shell carbon which had (before washing) an ash content of
20 about 2.3 weight percent; or Carbon B, a 4 x 8 mesh (about 4.7 mm x 2.4 mm) commercial grade coconut shell carbon which had (before washing) an ash content of about 2.6 weight percent. After water washing, Carbon A had an ash content of about 1 weight percent, and after
25 HCl acid washing, Carbon A had an ash content of about 0.2 weight percent. After HCl acid washing, Carbon B had an ash content of less than about 0.1 weight percent.

EXAMPLE 1



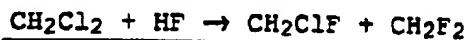
The reactor was charged with a 6% CrCl₃ on HCl-washed coconut Carbon A (30 mL, 14.7 g) catalyst and the catalyst was activated according to the Activation Procedure above. The reaction temperature was varied
35 from 200 to 275°C, the molar ratio of HF to CH₂Cl₂ was

varied from 2:1 to 6:1 and the contact time was 30 seconds in all cases. The reaction effluent was analyzed according to the Analytical Procedure above. The reaction results are shown in Table 1.

5

TABLE 1

| Run Time (Hours) | Temp. °C | Molar Ratio HF:CH ₂ Cl ₂ | %32 | %31 | %30 |
|---------------------|-------------|---------------------------------------------------|------|------|------|
| 1 | 275 | 4:1 | 49.1 | 13.5 | 37.4 |
| 5 | 250 | 4:1 | 45.9 | 12.6 | 41.5 |
| 21 | 225 | 4:1 | 45.2 | 11.7 | 43.1 |
| 24.5 | 200 | 4:1 | 15.2 | 12.9 | 72.0 |
| 31 | 250 | 6:1 | 55.8 | 12.2 | 32.0 |
| 35.5 | 250 | 2:1 | 26.4 | 11.8 | 61.8 |

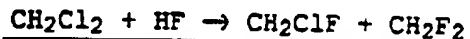
32 is CH₂F₂31 is CH₂ClF30 is CH₂Cl₂EXAMPLE 2

The reactor was charged with a 7.5% CrCl₃ on HCl-
 10 washed Carbon B (15 mL, 6.22 g) catalyst and the
 catalyst was activated according to the Activation
 Procedure above. The reaction temperature was varied
 from 200 to 275°C, the molar ratio of HF to halocarbon
 feed was varied from 2:1 to 6:1 and the contact time
 15 (C.T.) was varied from 2 to 30 seconds. The halocarbon
 feed consisted of 98.7 mole percent CH₂Cl₂ and 1.3 mole
 percent CH₂ClF. The reaction effluent was analyzed
 according to the Analytical Procedure above. The
 reaction results, in mole percent, are shown in Table 2.

20

TABLE 2

| Run Time (Hours) | Temp. °C | Molar Ratio HF:CH ₂ Cl ₂ | C.T. Seconds | %32 | %31 | %30 |
|---------------------|-------------|---------------------------------------------------|-----------------|------|------|------|
| 13.0 | 200 | 2:1 | 15 | 2.2 | 7.6 | 90.2 |
| 23.5 | 225 | 2:1 | 15 | 33.3 | 12.0 | 54.6 |
| 37.0 | 225 | 4:1 | 15 | 50.1 | 12.1 | 37.7 |
| 45.0 | 250 | 4:1 | 15 | 53.5 | 13.0 | 33.5 |
| 60.0 | 250 | 2:1 | 15 | 34.0 | 13.1 | 53.0 |
| 68.5 | 275 | 2:1 | 15 | 34.3 | 14.1 | 51.6 |
| 72.5 | 275 | 4:1 | 15 | 60.8 | 13.4 | 25.9 |
| 88.0 | 275 | 4:1 | 30 | 59.7 | 13.4 | 26.8 |
| 92.0 | 275 | 4:1 | 5 | 52.6 | 14.0 | 33.4 |
| 94.0 | 275 | 6:1 | 5 | 65.8 | 12.6 | 21.7 |
| 95.5 | 275 | 6:1 | 2 | 55.2 | 13.2 | 31.7 |

COMPARATIVE EXAMPLE A

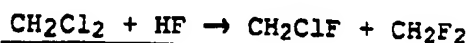
The reactor was charged with a 7.5% CrCl₃ on
 5 Carbon A (15 mL, 6.4 g) catalyst, which was not acid-
 washed. The catalyst was then activated according to
 the Activation Procedure above. The reaction
 temperature was varied from 200 to 275°C, the molar
 ratio of HF to CH₂Cl₂ was varied from 2:1 to 4:1 and the
 10 contact time was 15 seconds in all cases. The CH₂Cl₂
 feed to the reactor contained 98.9% CH₂Cl₂ and 1.1%
 CH₂ClF. The reaction effluent was analyzed according to
 the Analytical Procedure above. The reaction results
 are shown in Table A. Comparison of the results in
 15 Table A with results using the same temperature and
 ratio of HF to CH₂Cl₂ in Table 2 illustrates the
 superior results obtainable with low-ash content carbon.
 Comparison of the results in Table A with results using
 the same temperature and HF to CH₂Cl₂ in Table 1
 20 illustrates superior results using low-ash content

carbon containing even lesser amounts of trivalent chromium.

TABLE A

| Run Time (Hours) | Temp. °C | Molar Ratio HF:CH ₂ Cl ₂ | %32 | %31 | %30 |
|---------------------|-------------|---------------------------------------------------|------|------|------|
| 19.0 | 200 | 2:1 | 0.2 | 2.9 | 96.9 |
| 43.0 | 260 | 2:1 | 20.5 | 12.3 | 67.2 |
| 45.0 | 275 | 2:1 | 25.6 | 12.6 | 61.8 |
| 46.0 | 275 | 4:1 | 37.0 | 13.4 | 49.6 |
| 49.0 | 250 | 4:1 | 13.0 | 13.6 | 73.5 |
| 50.0 | 225 | 4:1 | 1.2 | 6.2 | 92.6 |

5

COMPARATIVE EXAMPLE BCatalyst Preparation

A quartz tube was charged with 400 g of Carbon A. The carbon was washed with de-ionized water at a flow rate of 40 mL/min at room temperature for 72 hours. The carbon granules were then dried at 150°C for 60 hours in air to obtain 373 g of dried granules. The ash content of this water washed carbon was about 1 weight percent.

A solution of CrCl₃•6H₂O (3.15 g) in de-ionized water (50 mL) was prepared in a round-bottomed flask. To this solution was added a portion (25.0 g) of the water washed carbon prepared as described above. The slurry was stirred on a rotary evaporator at room temperature at ambient pressure for 2 hours. The water was then removed under vacuum and the granules dried at 130°C in nitrogen for 20 hours. The recovered catalyst weighed 26.65 g and contained about 7.5 weight percent CrCl₃.

Fluorination

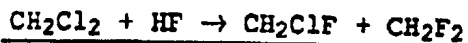
The reactor was charged with a 7.5% CrCl₃ on water washed Carbon A (15 mL, 6.92 g) catalyst prepared as

described above; and the catalyst was then activated according to the Activation Procedure above. The reaction temperature was varied from 200 to 300°C, the molar ratio of HF to CH₂Cl₂ was varied from 2:1 to 4:1 and the contact time was 15 seconds in all cases. The CH₂Cl₂ feed to the reactor contained 98.7% CH₂Cl₂ and 1.3% CH₂ClF. The reaction effluent was analyzed according to the Analytical Procedure above. The reaction results are shown in Table B. Comparison of the results in Table B with results in Table 1 and Table 2 illustrate the superior results obtainable using low-ash content carbon in accordance with this invention.

TABLE B

| Run Time (Hours) | Temp. °C | Molar Ratio HF:CH ₂ Cl ₂ | %32 | %31 | %30 |
|---------------------|-------------|---------------------------------------------------|------|------|------|
| 5.0 | 250 | 2:1 | 33.7 | 13.2 | 53.1 |
| 18.0 | 200 | 4:1 | 3.4 | 11.0 | 85.6 |
| 37.0 | 225 | 2:1 | 28.6 | 12.4 | 58.9 |
| 52.0 | 225 | 4:1 | 35.5 | 13.6 | 50.7 |
| 66.0 | 250 | 4:1 | 56.0 | 13.7 | 30.1 |
| 73.0 | 300 | 4:1 | 53.6 | 15.7 | 30.4 |

EXAMPLE 3



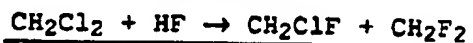
The reactor was charged with a 10% CrCl₃ on HCl-washed Carbon B (15 mL, 6.5 g) catalyst and the catalyst was activated according to the Activation Procedure above. The reaction temperature was varied from 200 to 250°C, the molar ratio of HF to CH₂Cl₂ was varied from 1:1 to 2:1 and the contact time was varied from 5 to 15 seconds. The CH₂Cl₂ feed to the reactor contained 98.9% CH₂Cl₂ and 1.1% CH₂ClF. The reaction effluent was

analyzed according to the Analytical Procedure above.
The reaction results are shown in Table 3.

TABLE 3

| Run Time (Hours) | Temp. °C | Molar Ratio HF:CH ₂ Cl ₂ | C.T. Sec. | %32 | %31 | %30 |
|---------------------|-------------|---------------------------------------------------|--------------|------|------|------|
| 4.0 | 200 | 2:1 | 15 | 8.4 | 11.2 | 80.5 |
| 7.0 | 225 | 2:1 | 15 | 25.7 | 10.7 | 63.6 |
| 26.0 | 215 | 2:1 | 15 | 27.0 | 10.5 | 62.4 |
| 31.0 | 210 | 2:1 | 15 | 23.5 | 10.8 | 65.7 |
| 33.0 | 205 | 2:1 | 15 | 13.3 | 10.5 | 76.2 |
| 35.5 | 225 | 1:1 | 5 | 13.6 | 9.1 | 77.3 |
| 38.0 | 225 | 2:1 | 5 | 25.1 | 11.0 | 63.9 |
| 39.5 | 250 | 2:1 | 5 | 27.2 | 11.8 | 61.1 |

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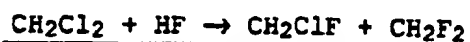
EXAMPLE 4

The reactor was charged with a 20% CrCl₃ on HCl-washed Carbon B (15 mL, 6.6 g) catalyst and the catalyst was activated according to the Activation Procedure
10 above. The reaction temperature was varied from 185 to 250°C, the molar ratio of HF to CH₂Cl₂ was varied from 1.5:1 to 2:1 and the contact time was varied from 5 to 15 seconds. The CH₂Cl₂ feed to the reactor contained 98.9% CH₂Cl₂ and 1.1% CH₂ClF. The reaction effluent was
15 analyzed according to the Analytical Procedure above. The reaction results are shown in Table 4.

TABLE 4

| Run Time (Hours) | Temp. °C | Molar Ratio HF:CH ₂ Cl ₂ | C.T. Sec. | %32 | %31 | %30 |
|---------------------|-------------|---------------------------------------------------|--------------|------|------|------|
| 17.0 | 200 | 2:1 | 15 | 24.5 | 10.3 | 65.2 |
| 18.0 | 185 | 2:1 | 15 | 4.4 | 9.4 | 86.2 |
| 21.5 | 225 | 2:1 | 5 | 28.1 | 10.9 | 61.0 |
| 22.5 | 250 | 2:1 | 5 | 27.2 | 11.7 | 61.1 |
| 23.5 | 250 | 1.5:1 | 5 | 20.7 | 10.9 | 68.4 |

EXAMPLE 5



The reactor was charged with a 60% CrCl₃ on HCl-
 5 washed Carbon B (15 mL, 9.0 g) catalyst and the catalyst
 was activated according to the Activation Procedure
 above. The reaction temperature was varied from 150 to
 200°C, the molar ratio of HF to CH₂Cl₂ was 2:1 and the
 contact time was 15 seconds. The CH₂Cl₂ feed to the
 10 reactor contained 98.9% CH₂Cl₂ and 1.1% CH₂ClF. The
 reaction effluent was analyzed according to the
 Analytical Procedure above. The reaction results are
 shown in Table 5.

TABLE 5

| Run Time (Hours) | Temp. °C | %32 | %31 | %30 |
|---------------------|-------------|------|------|------|
| 17.0 | 200 | 29.2 | 9.9 | 60.8 |
| 20.5 | 150 | 4.2 | 9.7 | 86.1 |
| 22.5 | 160 | 13.3 | 11.1 | 75.6 |
| 24.0 | 165 | 18.6 | 9.5 | 71.9 |
| 25.0 | 170 | 22.2 | 8.5 | 69.3 |
| 34.5 | 175 | 17.8 | 10.4 | 71.8 |
| 101 | 175 | 20.1 | 9.8 | 70.1 |
| 133 | 175 | 26.7 | 8.8 | 64.5 |

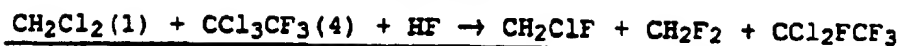
EXAMPLE 6

The reactor was charged with a 7.5% CrCl_3 on HCl-washed Carbon B (15 mL, 6.22 g) catalyst and the catalyst was activated according to the Activation Procedure above. The reaction temperature was varied from 275 to 350°C, and the contact time was varied from 5 to 15 seconds. The organic feed to the reactor consisted of 81.3 mole % CH_2Cl_2 and 18.2 mole % CCl_3CF_3 with the rest consisting essentially of 0.4 mole % CHCl_2F . The molar ratio of HF to the approximately 4:1 molar ratio mixture of CH_2Cl_2 : CCl_3CF_3 was varied from 1.7:1 to 8:1. The reaction effluent was analyzed according to the Analytical Procedure above. The reaction results in mole% are shown in Table 6.

TABLE 6

| R.T. (Hrs) | T °C | Molar Ratio HF:(32+113a) | C.T. Sec. | 23 | 32 | 31 | 30 | 114a | 123 | 113a |
|---------------|---------|-----------------------------|--------------|-----|------|------|------|------|-----|------|
| 1.0 | 300 | 1.7:1 | 14 | 1.4 | 30.8 | 12.4 | 37.3 | 2.7 | 2.5 | 12.7 |
| 5.0 | 300 | 1.7:1 | 14 | 1.8 | 31.7 | 12.0 | 34.3 | 2.5 | 1.8 | 15.6 |
| 12.0 | 325 | 3.5:1 | 14 | 3.4 | 45.0 | 11.4 | 19.0 | 8.3 | 3.4 | 9.1 |
| 28.0 | 325 | 1.7:1 | 14 | 4.7 | 24.6 | 12.0 | 38.9 | 4.4 | 4.2 | 10.8 |
| 33.0 | 350 | 1.7:1 | 14 | 9.2 | 23.4 | 12.1 | 36.1 | 6.1 | 6.5 | 5.5 |
| 37.0 | 350 | 4:1 | 15 | 6.3 | 44.9 | 11.3 | 16.1 | 10.0 | 5.6 | 4.9 |
| 56.0 | 275 | 4:1 | 5 | 0.1 | 47.3 | 10.2 | 20.6 | 0.3 | 0.2 | 21.2 |
| 58.0 | 300 | 4:1 | 5 | 0.4 | 48.5 | 10.8 | 18.4 | 0.8 | 0.6 | 20.3 |
| 60.0 | 350 | 4:1 | 5 | 2.6 | 45.6 | 12.0 | 18.1 | 4.7 | 2.8 | 13.7 |
| 76.0 | 350 | 8:1 | 15 | 4.2 | 56.8 | 8.9 | 7.9 | 12.3 | 4.1 | 4.9 |
| 79.0 | 325 | 8:1 | 15 | 2.3 | 60.4 | 8.8 | 7.4 | 6.2 | 2.6 | 12.0 |

23 is CHF_3 114a is CCl_2FCF_3 123 is CHCl_2CF_3 113a is CCl_3CF_3

EXAMPLE 7

The reactor was charged with a 7.5% CrCl_3 on HCl-washed Carbon B (15 mL, 6.22 g) catalyst and the catalyst was activated according to the Activation Procedure above. The reaction temperature was 300°C, and the contact time was 18 seconds. The organic feed to the reactor consisted of 21.1 mole % CH_2Cl_2 and 78.1 mole % CCl_3CF_3 with the rest consisting essentially of 0.2 mole % CHCl_2F and 0.4 mole % CCl_2FCF_3 . The molar ratio of HF to the approximately 1:4 molar ratio mixture of CH_2Cl_2 : CCl_3CF_3 was 4:1. The reaction effluent was analyzed according to the Analytical Procedure above. The reaction results in mole % are shown in Table 7.

TABLE 7

| R.T. (Hrs) | T °C | C.T. Sec | %23 | %32 | %31 | %30 | %114a | %123 | %113a |
|---------------|---------|-------------|-----|------|-----|-----|-------|------|-------|
| 2.0 | 300 | 18 | 0.2 | 13.8 | 1.4 | 1.0 | 7.3 | 0.7 | 75.4 |
| 19.0 | 300 | 18 | 0.1 | 13.2 | 1.3 | 0.8 | 7.3 | 0.4 | 76.6 |

What is claimed is:

1. A process for producing difluoromethane comprising the steps of contacting a gaseous mixture containing CH_2Cl_2 and HF with a catalyst containing a catalytically effective amount of trivalent chromium supported on a carbon having an ash content less than 0.5 weight percent, at a temperature of from about 180°C to about 375°C .
2. The process of Claim 1 wherein the carbon is acid-washed.
3. The process of Claim 1 or Claim 2 wherein the catalyst is selected from those wherein a carbon support contains chromium chloride, fluorided chromium chloride, or mixtures of chromium chloride and chromium fluoride.
4. The process of Claim 3 wherein the chromium content expressed as CrCl_3 is from about 5 to 60 weight percent of the carbon supported catalyst.
5. The process of Claim 3 wherein the starting material to be fluorinated consists essentially of CH_2Cl_2 and molar ratio of HF to CH_2Cl_2 is from about 0.5:1 to 10:1.
6. The process of Claim 1 or Claim 2 wherein the gaseous mixture further contains CCl_3CF_3 ; wherein the molar ratio of CH_2Cl_2 to CCl_3CF_3 in the gaseous mixture ranges from about 1:9 to 9:1; and wherein $\text{CF}_3\text{CCl}_2\text{F}$ is produced.
7. The process of Claim 1 or Claim 2 wherein CH_2ClF is produced; and wherein CH_2ClF is recycled as an azeotrope with HF, said azeotrope containing from about 58 to 65 mole percent CH_2ClF .
8. The process of Claim 1 or Claim 2 wherein unreacted CH_2Cl_2 is recycled as an azeotrope with HF, said azeotrope containing from about 5 to 29 mole percent CH_2Cl_2 .